



A comprehensive kinetic, thermodynamic and photochemical study of some spiro-indoline-oxazines

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Abstract. The thermoreversible photochromic reaction of spiro-indoline-oxazines to photomerocyanines has been studied by stationary spectrophotometric techniques. Two methods are described for determining the molar absorption coefficient of the metastable photomerocyanine and the quantum yield of the colour-forming photoreaction. Kinetic parameters (reaction rate and activation energy) and thermodynamic quantities (equilibrium constant and enthalpy) of the thermal reaction have also been determined. Based on the results obtained, some general correlations between the structure of these molecules and their photochromic and thermochromic properties have been drawn.

Keywords. Spiro-indoline-oxazines; photomerocyanines; thermochromism; photochromism; photokinetics.

1. Introduction

Photochromism, that is the photoinduced reversible transformation of a chemical species into another one having a different absorption spectrum, has raised great interest over the last decade because of the multiplicity of actual or potential applications (Guglielmetti 1990). Photochromic systems can be used as optical filters, optical switches, temporary or permanent memories, and also as coating materials and temperature indicators, just to mention a few applications. Depending on the specific application, different thermal and photochemical properties are required. Therefore, it is clear that the thermal rate constants and the photochemical quantum yields of photochromic reactions have to be determined as exactly as possible.

An empirical quantity which has often been employed to represent the goodness of a photochromic system is colourability, that is, the propensity of the colourless molecule to be transformed into the coloured species under irradiation. It has often been expressed as the apparent molar absorption coefficient of the coloured form attained under fixed experimental conditions.

In this work, some spiro-indoline-oxazine (SO, colourless) and photomerocyanine (PM, coloured) systems were investigated in polar and nonpolar solvents. For these molecules, the photochromism is due to photocleavage of the spiro-bond of the SO under UV irradiation to give the open PM structure which absorbs in the visible region. Our aim was to answer several questions:

- What is the colour of **PM** and how is it influenced by structural and environmental factors?
- How important is thermochromism and how is it affected by the solvent and structure?
- How fast is the thermal bleaching and how temperature-dependent is it?
- Is it possible to give a quantitative evaluation of "colourability" under either pulsed or steady state irradiation?

Answering these questions well helps to attain complete understanding of the photochromic properties of these molecules. This requires determining solvent spectral shifts of the **PM** colour absorption band (solvatochromism), measuring thermodynamic quantities (equilibrium constant, enthalpy, entropy) and kinetic parameters (rate coefficient, activation energy, frequency factor) of the reaction, evaluating the PM molar absorption coefficient and the photoreaction quantum yield and studying the mechanisms of the photodegradative processes. The results obtained for a series of SO's give an overall picture of the physicochemical and photophysical properties of these systems and help to find criteria to test them with respect to potential applications.

2. Experimental

2.1 Materials

The photochromic molecules studied (supplied by Great Lakes Chemical Italia S.r.l) were seven spiro-indoline-oxazines, with different aryl groups linked to the oxazine moiety (naphtho, N; phenanthro, P; benzo, B) and/or different substituents on each moiety. The structures and symbols of the molecules are shown in figure 1. In the symbols, the substituents on the indoline and oxazine moiety precede and follow, respectively, the bold-face letter representing the aryl group.

The solvents, ethanol (EtOH) and methylcyclohexane (MCH), were reagent grade Carlo Erba products. EtOH was used without further purification while MCH was treated according to standard procedures.

2.2 Equipment

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer or on a Beckman diode array DU 7500 spectrophotometer. For varying temperature, a cryostat (Oxford Instruments) was used, equipped with a temperature controller operating between 77 K (if liquid nitrogen was used for cooling) and 500 K. The temperature precision was within $\pm 1^\circ\text{C}$; the accuracy in the temperature control was of the order of \pm

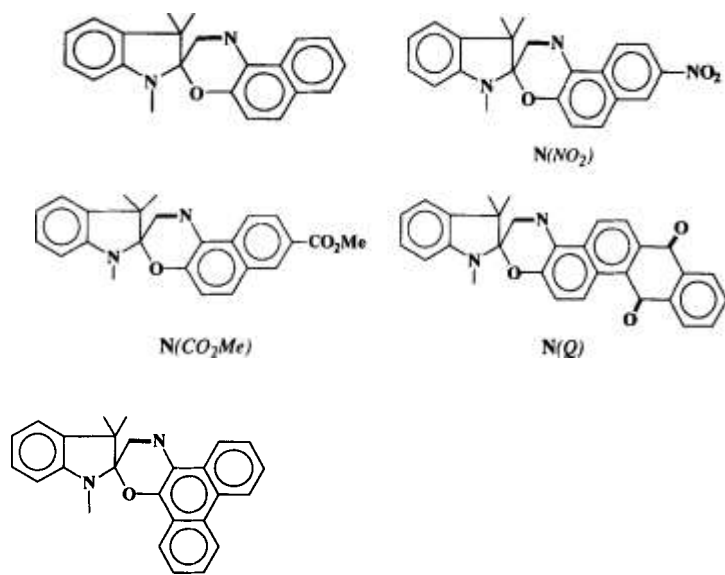
0.2 C. A 250 W medium pressure mercury lamp filtered by an interference filter ($\lambda = 336 \text{ nm}$) was used for producing the coloured **PM** form. Irradiation intensity, which was constant during each run, was determined using potassium ferrioxalate actinometry (typically, $10^{-6} \text{ einstein dm}^{-2} \text{ s}^{-1}$).

2.3 Measurement conditions

2.3a Thermo-equilibrium measurements:

To observe the thermal equilibrium, the concentrations of the starting **SO** were kept as high as possible (10^{-3} to $10^{-4} \text{ mol dm}^{-3}$). The solutions were spectrophotometrically analysed in the visible absorption region of the open form, in the temperature range 290-320 K.

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2.3b Photokinetic measurements:

The concentrations of the starting **SO** were of the order of $(1 \text{ to } 5) \times 10^{-5} \text{ M}$, corresponding to absorbances in the range 0.1 - 0.3 at the irradiation wavelength (366 nm). The light exposure of the sample (1-cm path cell, 1 cm^3 of solution) was carried out in the spectrophotometer holder at right angles to the analysis light. The increase of the **PM** absorbance was followed, under stationary irradiation, at the absorption maximum wavelength (550-620 nm), where the excitation light did not disturb the absorbance measurement, up to photostationary state attainment. Spectral changes were recorded at constant temperature and repeated on the same solution at temperature intervals of 3-4 C in a

temperature range of about 30 °C, which was chosen within 260 and 305 K, depending on the molecule. To assure the attainment of the thermal equilibrium, about half an hour elapsed after resetting the temperature control.

The kinetic rate parameters of the ring-closure reaction were determined at each temperature, following the disappearance of the coloured form at the wavelength of maximum absorbance, after having removed the irradiating source. First-order rate constants were obtained from linear log *A* vs. time plots (correlation coefficient greater than 0.99, using about 100 experimental points). The activation energies and frequency factors of the thermal back reactions were determined from Arrhenius plots. An uncertainty of about 10% was evaluated for the activation energy, while the frequency factor was affected by more than 50% uncertainty.

3. Results and discussion

Evaluating the thermochromic and photochromic properties of the SO molecules investigated requires the determination of the concentration of PM (thermally or photochemically produced). Obviously, the simplest way for determining the concentration of the coloured form would be through its absorbance, if the molar absorption coefficient (ϵ_{PM}) were known. However, determining ϵ_{PM} is a non-trivial problem (Fischer 1967; Rau 1984, 1991; Micheau and Lavabre 1986; Wilkinson *et al* 1992; Pimienta *et al* 1994). The difficulty arises because the coloured species (**PM**), produced under UV irradiation, reconverts to the colourless molecule (SO) within a few seconds. To avoid the thermal back reaction, the most frequently employed methods have been the saturation method, using an exciting flash and times of analysis very much shorter than the PM lifetime, and the low temperature method, producing the PM with steady irradiation and assuming a complete SO → PM photoconversion. Each of these procedures has some disadvantages; the first one because of using very intense pulsed irradiating light, with the possibility of side photoreactions, local heating and inhomogeneity and the second one because it requires a low temperature which is far from those of operational interest.

3.1 Photochromism

3.1a Determination of the quantum yields and molar absorption coefficients: For the systems under study, for which the quantum yield of the reverse photoreaction is assumed negligible (Wilkinson *et al* 1992), the kinetic equation can be written in terms of molar absorption coefficient (ϵ_{PM}) and time dependence of the photomerocyanine absorbance (APM) at the measurement wavelength:

$$\frac{dAPM}{dt} = \epsilon_{PM} I_{SO} - k_1 A_{PM}$$

*I*_{SO} represents the intensity of the monochromatic excitation light absorbed by SO per time-unit (einstein dm⁻³ s⁻¹). Since PM also absorbs the excitation light ($\lambda_{exc} = 366$ nm), the fraction *I*_{SO}/*I* (*I* represents the total absorbed light) has to be accounted for. By expressing the

total absorbed light, I , as $J^0 [1 - \exp(-2.3A')]J$ (the prime superscript is used for absorbances and molar absorption coefficients at A_{exc}), the following relationship is obtained:

$$\frac{dA_{PM}}{dt} = \epsilon_{PM} J^0 F A' - k_4 A_{PM} \quad (2)$$

where $F = [1 - \exp(-2.3A')]/A'$ represents the photokinetic factor (Bar and Gauglitz

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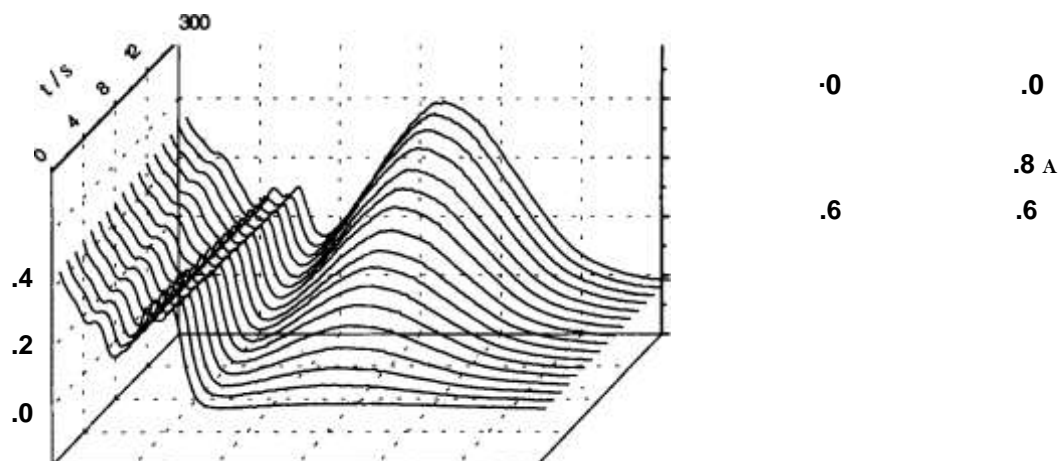


Figure 2. Time course of the photocoloration reaction for $N(NO_2)$ in MCH at 293 K (from Favaro et al 1994, 1995).

1989; Borderie **et al** 1992; Gauglitz and Scheerer 1993), which depends on the degree of photoconversion.

When the photostationary state is attained, namely $dA_{PM}/dt = 0$, the PM absorbance has reached its limiting value at the temperature of experiment (A_{PM}^{∞});

$$\epsilon_{PM} \Phi I^0 F^{\infty} A_{SO}^{\infty} = k_4 A_{PM}^{\infty} \quad (3)$$

Superscripts ∞ refer to photostationary conditions. Spectrophotometrically following the time course of the reaction promoted by steady state irradiation provides A_{PM} values as a function of time and its limiting value, A_{PM}^{∞} . A typical reaction course obtained under steady irradiation is shown in figure 2. The bleaching rate coefficient, k_4 , can be measured with very high precision from the first order kinetic treatment of the absorption decay curve obtained when the irradiating source was removed; ϵ_{PM}^{∞} .

$\langle I \rangle$ and F^m are unknown. The above rate equations, which take into account the superposition of the thermal and photochemical steps, show a very high sensitivity to numerical instability (Bar and Gauglitz 1989; Borderie **et al** 1992). Therefore, very accurate experimental data are needed and they have to be taken in appropriate conditions, that is, the irradiation time required to attain the photostationary state should be as similar as possible to the time of bleaching (Bar and Gauglitz 1989; Borderie **et al** 1992; Gauglitz and Scheerer 1993). Here, we propose two methods for treating spectrophotometric results of thermoreversible photoreactions, by which two different types of data sets were used: by the first method, (a) limiting absorbances and bleaching rate parameters were recorded at different temperatures (Favaro **et al** 1995); by the second method, (b), absorbance/time values were measured at constant temperature.

(i) Method (a) - This method has some aspects in common with that developed by Gauglitz and Sheerer (1993) who obtained from (1) a relationship between the maximum absorbance at the photostationary state with the temperature dependence of the thermal back reaction ($k_{11} = k_0 \exp(-E_0/RT)$). In this way, they used absorbance as the dependent variable and temperature as the independent variable, obtaining an exponential curve from which they determined the unknown parameters by a fitting procedure. By our method, the variables are A and k_{11}/F and a linear fitting allows the unknown parameters to be obtained. To apply this procedure, (3) is rearranged, substituting the instantaneous SO concentration as a function of the PM concentration and initial SO concentration (C_0),

$A;_0 = i;_0 [SO] =_0 (C_0 - [PM]) = i;_0 (C_0 - (A_{PM}/\epsilon_{PM}))$, thus obtaining:

A linear relationship between $1/A$ and k_{11}/F^0 is thus obtained which allows $i;_{PM}$ to be evaluated from the intercept and cf from the intercept to slope ratio. The photokinetic factor, F , which varies during the reaction course, attains a constant value at the photostationary state, which depends on temperature because of the temperature effect on the degree of photoconversion. The problem can be solved by an iterative method, starting from an approximate PM concentration determined from the visible spectrum, where only PM absorbs, and using it to calculate an approximate F^0 value. By inserting this value in (4) an approximate $i;_{PM}$ is extrapolated. Extrapolations of $i;_{PM}$ and recalculation of the corresponding F^0 are iterated until the intercept (4) corresponds to the given $(i;_{PM} C_0)^{-1}$. Once $i;_{PM}$ has been determined, the quantum yield can be obtained from the intercept to slope ratio of the linear plot (4) or, alternatively, from (5) by extrapolating the colour-forming rate at zero time:

$$cf = \left(\frac{dM}{dt} \right)_{t=0} / [1,_{PM} J^0 \{t - \exp(-2.3A)\}].$$

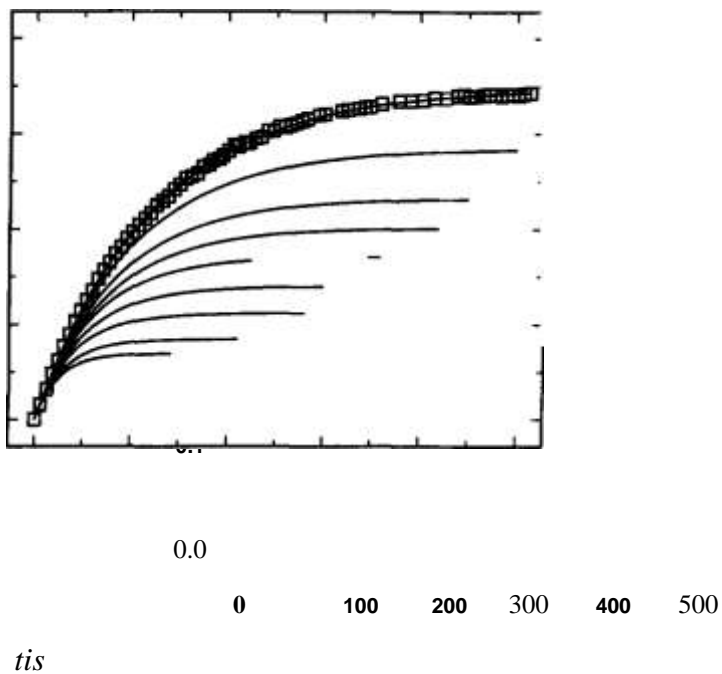


Figure 3. Time dependence of the colour-forming process under steady irradiation at various temperatures for (N-Et)N in MCH (from Favaro *et al* 1994, 1995).

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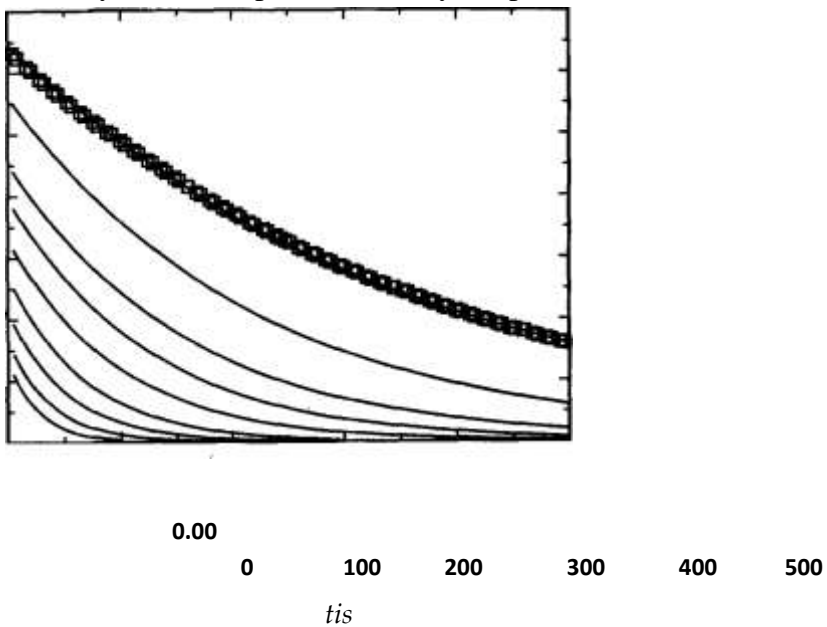


Figure 4. Kinetics of bleaching for (N-Et)N in MCH at various temperatures (from Favaro *et al* 1994, 1995).

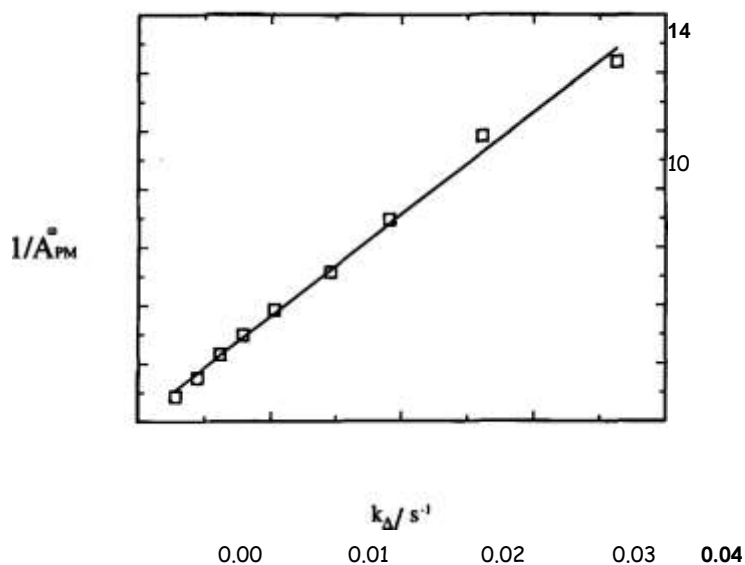


Figure 5. Data from figures 3 and 4 treated according to (4) (from Favaro *et al* 1994, 1995).

Examples of the experimental runs needed to apply the procedure described are shown in figure 3 (time dependence of colour forming at various temperatures) and figure 4 (corresponding bleaching kinetics). The linear (optimized) fitting of the experimental data (4) is shown in figure 5.

Method (b)-This method consists of the integration of the differential equation (2) to obtain a function $A_{PM}(t)$ describing the kinetics of the colour-forming reaction. However, the photokinetic differential equation cannot be solved in a closed form

because of the photokinetics factors, which varies during the reaction course. Only if the irradiation wavelength corresponded to an isosbestic point of the absorption spectra of SO and PM, would the photokinetic factors be rigorously constant. In general, for the systems under investigation, developing the exponential part of F into a series and truncating the development to the second term is an acceptable approximation. The following expression is obtained for F .

$$F = 2.303 (1 - 2.303/2A)$$

By inserting (6) in (2), (7) is obtained:

$$i_t dA_{PM}/dt = I X A^2 + /3A_{PM} + y,$$

The experimental points (absorbance/time value) are entered into the integrated curve (8): the and values, which are included as parameters in the equation, can be optimized so as to

minimize the interpolation errors. The X^2 minimization was achieved using the PC Mathematica package, based on the Levenberg-Marquardt method for nonlinear fitting calculations. Compared to method (a), this last procedure has the advantage of allowing the unknown parameters to be obtained from one experiment.. The most important point to obtain reliable results is determining the value to be inserted in (8) to numerical instability.

(Thermodynamic and photochemistry of spiro-indoline-oxazines between 0.1 and 1 and they are scarcely affected by solvent but are markedly affected by structure. Interestingly, the nitroderivative exhibits a high value in both solvents, which is probably due to the contribution from a triplet mechanism (Kellmann *et al* 1995). Bleaching rate parameters (k_1 and k_0) are reported in table 2. With some exceptions, $k_{1,..}$ values are higher in MCH than in EtOH; in the latter solvent, larger differences in $k_{1,..}$ are also observed between different molecules. The activation energies, obtained from Arrhenius plots (figure 6), are of the order of 70-100 kJ mol⁻¹ and are generally higher in a polar solvent. The k_0 values range on a very large interval (10^{11} - 10^{15} s⁻¹); despite their great uncertainty, the observed differences, due to both solvent and structure, are, at least qualitatively, meaningful.

3.2 Solvatochromism

In table 1, the wavelengths of the visible maximum absorptions are reported in parentheses in both the solvents explored. According to what has been previously

Table 1. Molar absorption coefficients (dm³ mol⁻¹ cm⁻¹) at A.max (nm, in parentheses) and quantum yields of the coloured forms in two solvents.

Compounds	EtOH		MCH		Av (cm ⁻¹)
	$\epsilon_{PM}(\max)$	ϕ	$\epsilon_{PM}(\max)$	ϕ	
N	61000(613)	0.32	38000(585)	0.41	780
(N-Et)N	53300(613)	0.42	50000(591)	0.46	607
N(CO ₂ Me)	48800(609)	0.36	45500(591)	0.35	500
(Me)zN(COEt)	42000(617)	0.23	65000(608)	0.14	240
N(Q)	6500(610)	0.16	39800(605)	0.73	135
N(NO ₂)	74200(610)	0.72	63700(605)		135
				HO	
(Me)z B(di-aza)	30500(591)	0.12	26800(581)	0.10	290
p	87000(600)	0.29	51000(566)	0.49	1000
(N-Pr)P	31000(595)	0.85	56000(574)	0.51	780

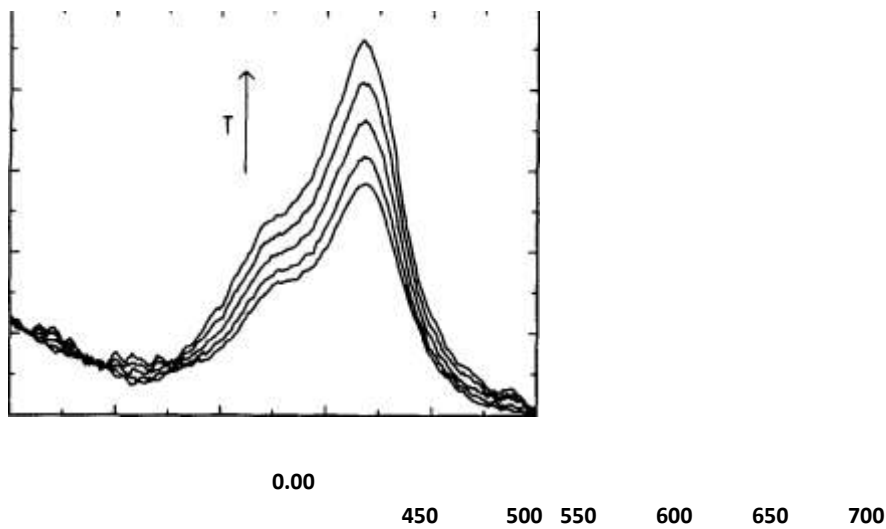


Figure 5. Thermochromism: absorption spectra of (Me)₂N(COEt) ($c = 3.5 \times 10^{-4} \text{ mol dm}^{-3}$) in EtOH; temperature range: 288-308 K (from Favaro *et al* 1994, 1995).

found for some other SO's (Favaro *et al* 1994), the molecules under study exhibit positive solvatochromism, that is, the maximum of the absorption band undergoes a red-shift from nonpolar to polar solvents (Jacques 1986): the observed shifts (cm^{-1}) are reported in table 1. This behaviour indicates that the excited state dipole moment is higher than the ground-state dipole moment; the larger this difference, the greater the spectral shift and more the ground-state weakly-polar molecule approaches the configuration of the quinoid form (Lenoble and Becker 1986). From the ϵ_{ν} values reported in the table, it can be seen that the sensitivity of the absorption

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maximum to the solvent effect markedly depends on structure. According to expectation, positive solvatochromism is not favoured by substituents which increase the contribution of zwitterionic forms to the resonance hybrid describing the ground-state molecule, that is, electron-attracting groups in the oxazine moiety. Negative solvatochromism, found for some nitro-spiropyranes (Keum *et al* 1991) which are molecules closely related in structure to those studied here, is in agreement with this view.

1.1 Thermochromism

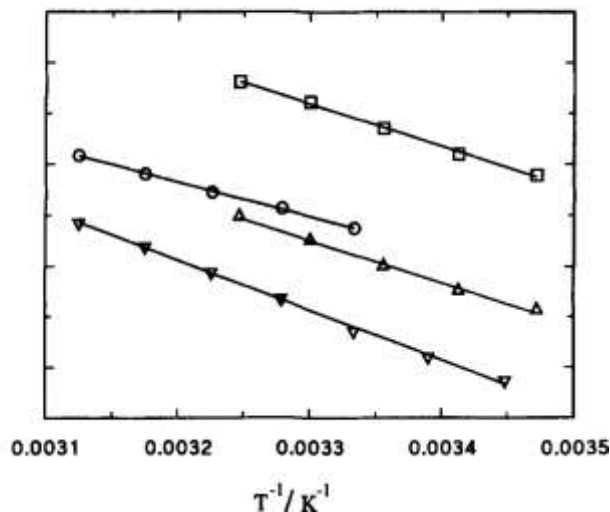
It is known that non-irradiated concentrated solutions of SO may show the absorption band in the visible region at room temperature, denoting that thermal equilibrium is established between the open and closed forms (Chu 1983; Pozzo *et al* 1993; Favaro *et al* 1995). In order to characterize the thermochromism of a molecular system, the parameters to be measured are the reaction enthalpy, which determines the chromatic sensitivity to temperature, and the equilibrium constant, which allows the colour intensity to be evaluated at each temperature. None of the molecules investigated exhibited observable thermochromism in MCH; only some of them exhibited thermochromism in the polar solvent EtOH. The absorption intensity in the visible region increased with temperature, as shown in figure 7.

The enthalpy of the reaction was determined by measuring the absorbance of the coloured form at several temperatures, according to the van't Hoff equation:

$$\frac{d \ln K}{d(T^{-1})} = \frac{d \ln A}{d(T^{-1})} = \frac{AH}{R} \quad (9)$$

The linearity of the $\ln A$ vs. T^{-1} plots is shown in figure 8. The equilibrium constant could be calculated from the absorbance of PM in the visible region and the measured ϵ_{PM} values:

$$K = \frac{[PM]}{[SO]} = \frac{A_{PM}/\epsilon_{PM}}{c_0 - A_{PM}/\epsilon_{PM}}$$



The K values of the reaction in EtOH at 298 K, together with the thermodynamic (ΔH^0 , ΔG^0 , ΔS^0) and kinetic (rate constant, k_t , and activation energy, E_0) parameters, are reported in table 3. The equilibrium constants range from 10^{-2} to 10^{-4} and are strongly structure-dependent. The percentage of coloured form present in thermal equilibrium depends

significantly on the contribution of zwitterionic structures to the resonance hybrid.

This contribution is favoured by electron-attracting substituents in the oxazine moiety and electron-donating substituents in the indoline moiety. At least one of these characteristics is present in the more markedly thermochromic molecules. Results from the literature are in line with this generalization: in a series of di-pyrido-oxazines, the equilibrium constant for a methoxy derivative has been found to have the highest value (Pozzo *et al* 1993).

As can be seen from the ΔH^0 values given in table 3, the reaction is endothermic by 10-20 kJ mol⁻¹: the lowest ΔH^0 values were reported for the phenanthromolecules. The ΔS^0 values are very low: they were determined as differences of two large and close numbers ($\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$), thus they are subject to large uncertainty. The small (positive or negative) entropy changes indicate that the reaction is almost isoentropic. This is due to partial balance between the positive contribution to entropy owing to the increased torsional freedom in the open structure and the negative contribution to entropy due to solvent reorganization around the more polar merocyanine form. From the thermodynamic data and the kinetic parameters of the bleaching reaction, the rate constants and the activation energies of the thermal breakage of the spiro-bond were obtained. The values reported in table 3 indicate that the activation energies range over 80-120 kJ mol⁻¹, the reaction rates vary over a very large interval (10⁻⁵-10⁻² s⁻¹), and that the frequency factors are consistent with those obtained from the back reaction. Considering the effect of the polar medium and that of substituents, the following generalization can be drawn: the driving force for thermochromism to be observed is the degree of stabilization of the PM by solvent polarity.

3.4 Thermo-colourability and photo-colourability

Qualitative definitions of photo-colourability of this kind of molecule have been previously proposed (Samat *et al* 1975, 1991; Appriou *et al* 1978; Gaude *et al* 1991; Gautron *et al* 1991; Eloy *et al* 1992), but not of thermo-colourability. The difficulties encountered in giving such definitions earlier derived mainly from the problem of the determination of ϵ_{PM} . From the results of this paper some criteria can be deduced to express both thermo- and photo-colourability quantitatively. Thermo-colourability

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increases with increasing temperature and can be defined at each temperature as the absorbance at the maximum of the PM band in the visible (A_{PM}) relative to the total concentration, c_0 . By rearranging (10) the following expression is obtained,

$$(11) \quad A_{PM}/c_0 = K \cdot \epsilon_{PM}/(K + 1),$$

which allows thermo-colourability of different molecules to be compared, if the parameters K

and ϵ_{PM} are known. In reality, since in the present cases $K_{298} \ll 1$, thermo-colourability is equal to the $K \cdot \epsilon_{PM}$ product.

For evaluating photo-colourability, pulsed and stationary irradiation conditions have to be distinguished (Favaro *et al* 1995). Under steady irradiation, the maximum colour intensity attainable increases as the temperature decreases because of the temperature dependence of the bleaching rate (figure 3). Colourability ($A/c0$) can be obtained from (4) and depends on $\epsilon_{PM} \cdot \langle I \rangle$ and $k_{1.}$. Upon pulsed excitation, the maximum colour intensity does not depend on temperature because the bleaching rate is negligible: in these conditions photo-colourability is proportional to the $\epsilon_{PM} \cdot \langle I \rangle$ product.

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